2012 TECHNICAL WORKSHOP

on Environment and Alternative Energy

Technical Sessions

Active Corrosion Protection of Sol-Gel Coatings on AA2024-T3

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OBJECTIVE

Development and implementation of industrial pre-treatments for aluminium alloys, using environmentally friendly substances and without danger to health, instead of pre-treatments based on chromium.

Field of Application:

Aluminium alloys with applications in aeronautics and aerospace industry.

AA 2024-T3 Aluminium Alloy

➔Light, with good uniform corrosion resistance and fatigue resistance.

➔Low pitting corrosion resistance.

➔Needs protection before use, e.g., paint application.

➔Application of paint requires:

- A resistant and stable interface, promoting adhesion between the paint and the substrate;

- For this purpose, surface pre-treatments are used, being traditionally based on chromate.

Cr(VI) Based coatings:

- Very good effectiveness-to-costs ratio
- **Self-healing ability**
- High toxicity

Health and Environmental Problems!!!

Alternatives to Chromium:

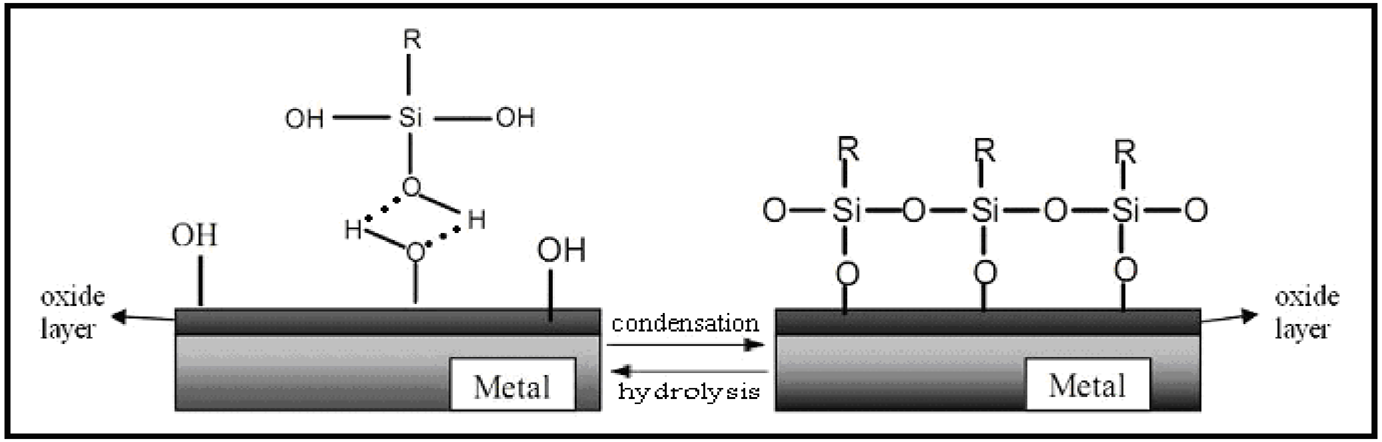
- Anodizing Treatment
- Silane Based Coatings
- Cerium Salt Based coatings
- **Sol Gel Coatings**

Sol Gel Coatings

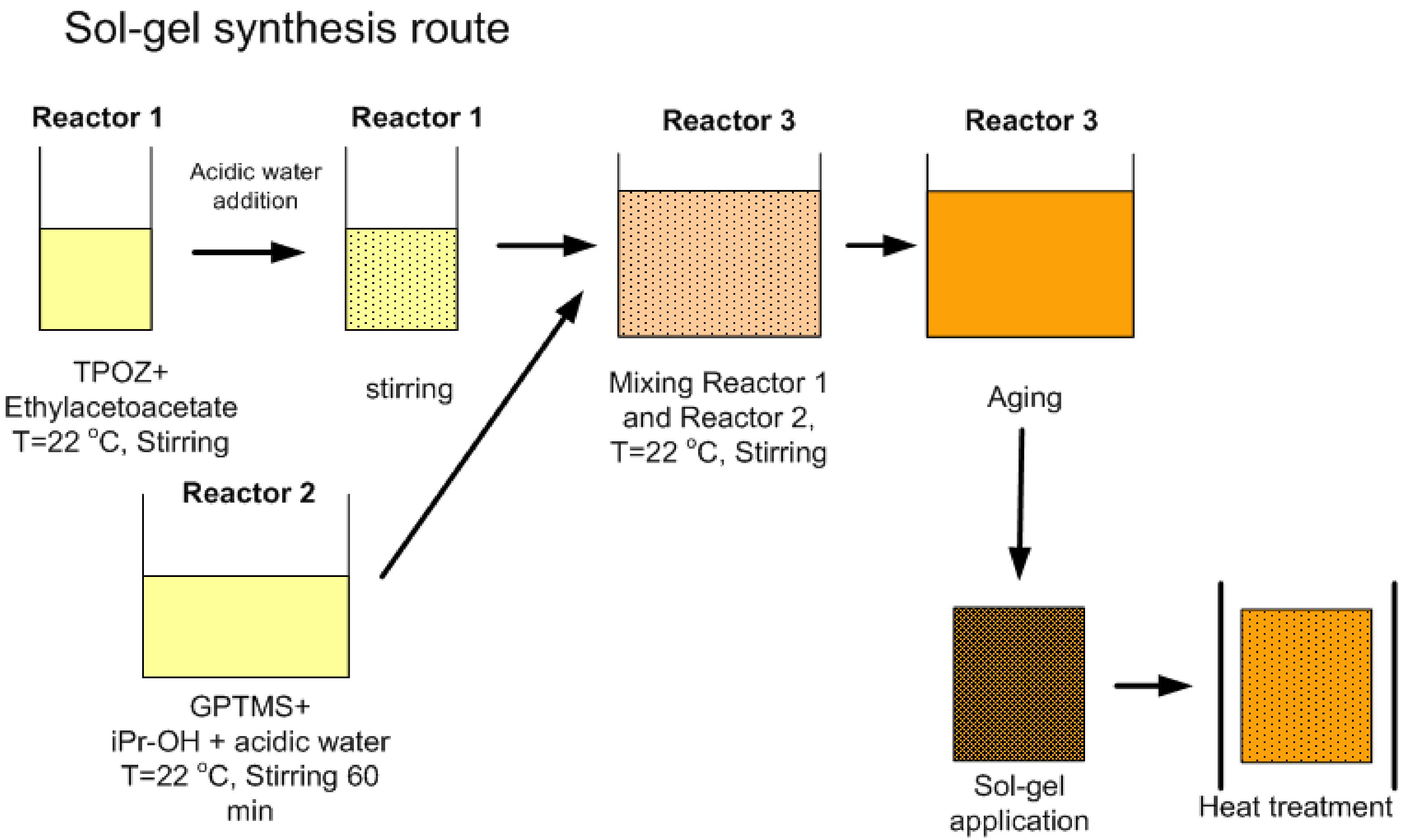
The sol-gel process involves the growth of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel).

The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water.

Sol-gel technique is depending on two steps hydrolysis and condensation reactions.



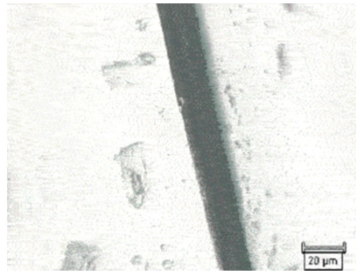
Sol-gel synthesis

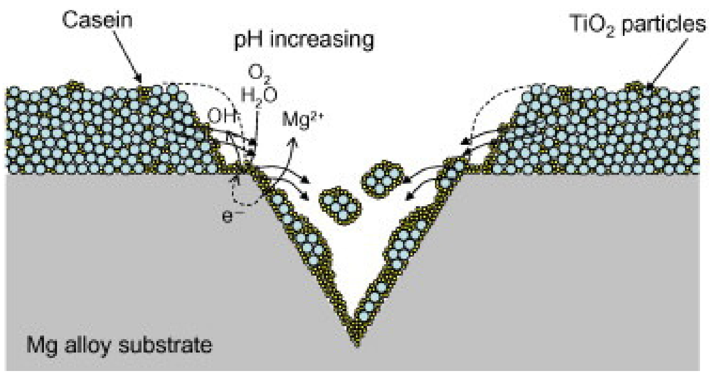


M.L. Zheludkevich et al. / Electrochimica Acta 51 (2005) 208–217

Active Corrosion Protection

Self-Healing in protective coatings is based on the complete coating recovery of the coating functionalities due to a real healing of the defect retrieving initial coating integrity.





The hindering of the corrosion activity in the defect by the coating itself employing any mechanisms can be already considered as self-healing, because the corrosion protective system recovers its main function, namely the corrosion protection, after being damaged

Akihiro Yabuki, , Mariko Sakai, Corros. Sci. 53 2 (2011) 829–833

Corrosion protection of metallic substrates

Passive corrosion protection	Active corrosion protection
Coatings	**Inhibiting species**
Aesthetic properties Tailored surface properties Good barrier against corrosive Species	Decrease of corrosion rate Self-healing of defects
Lack of self –healing	Added to corrosive medium

Passive + active

Coating + Corrosion Inhibitor

Combination of barrier and self-healing

- Negative effect of inhibitor on coating stability
- Deactivation of inhibitor on coating
- Uncontrollable release of inhibitor

Active Corrosion Protection

Direct incorporation of corrosion inhibitors in coating formulations can cause:

-**detrimental interaction** between inhibitors and coating matrix

-**spontaneous leaching** of inhibitors

Active agent must be encapsulated in order to prevent its interaction with components of coatings

Nanocontainers

-hosting structures for corrosion inhibitors

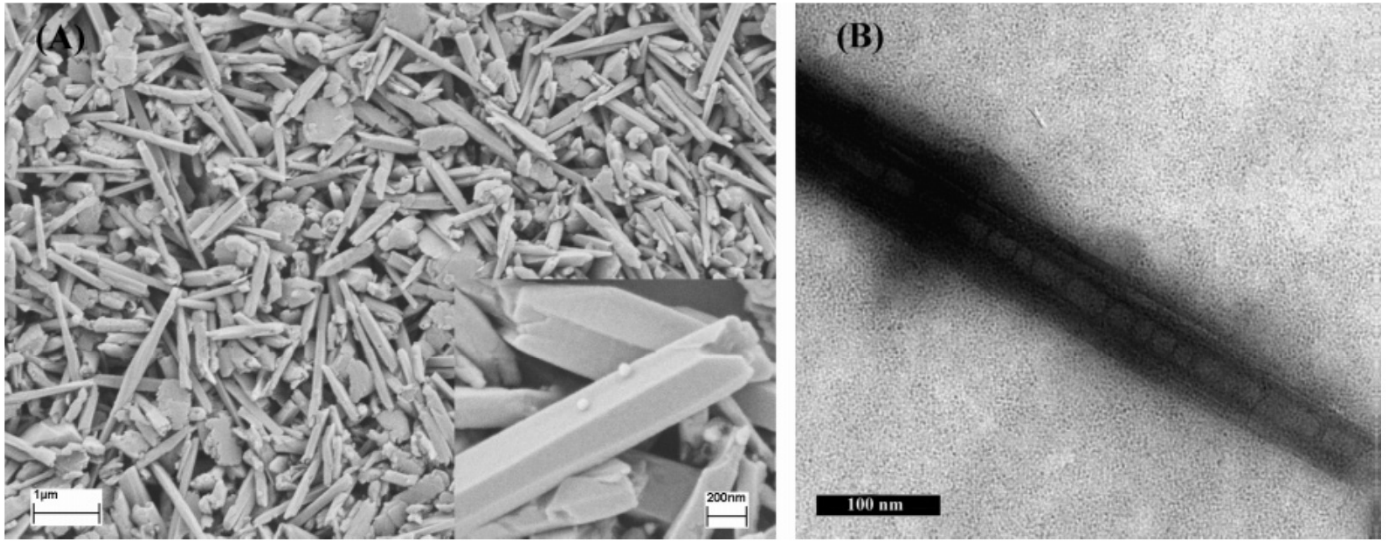
-ability to control the release of active species

Example 1: Halloysite Nanotubes

Halloysite is defined as a two-layered aluminosilicate, which has a hollow tubular structure in the submicrometer range.

The halloysite tubules are very small; typical size: less than 3.0 μm longx0.3 μm outer diameter and an inner diameter of 10-150 nm.

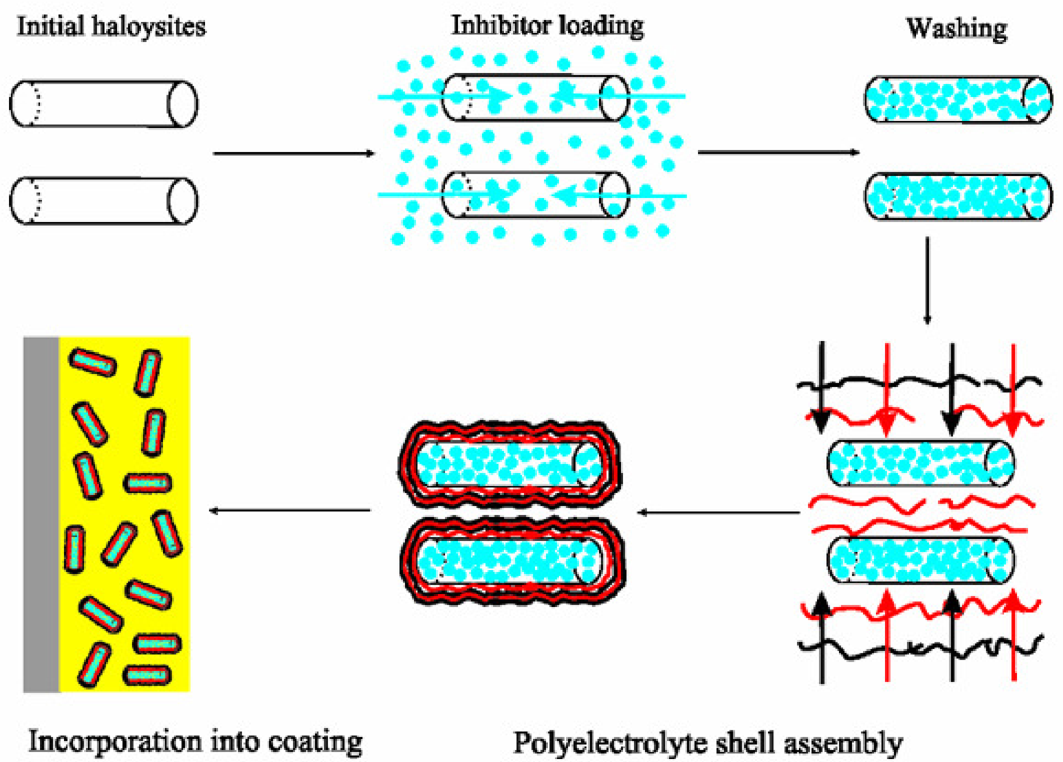
SEM



TEM

Dmitry G. Shchukin, S. V. Lamaka, K. A. Yasakau, M. L. Zheludkevich, M. G. S. Ferreira, and H. Mo1hwald, J. Phys. Chem. C 2008**,** *112,* 958-964

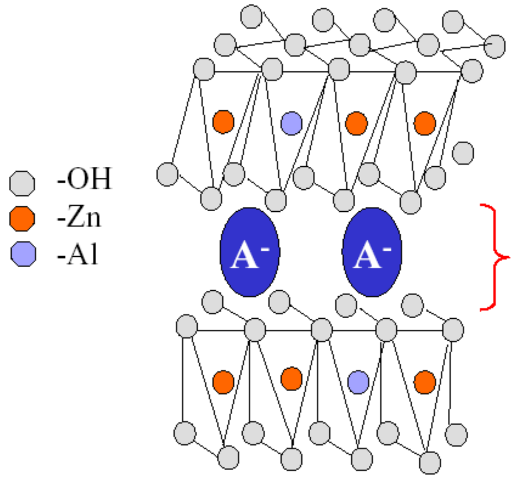
Halloysite as nanocontainers of corrosion inhibitor



Fabrication of 2-mercaptobenzothiazole-loaded halloysite/polyelectrolyte nanocontainers

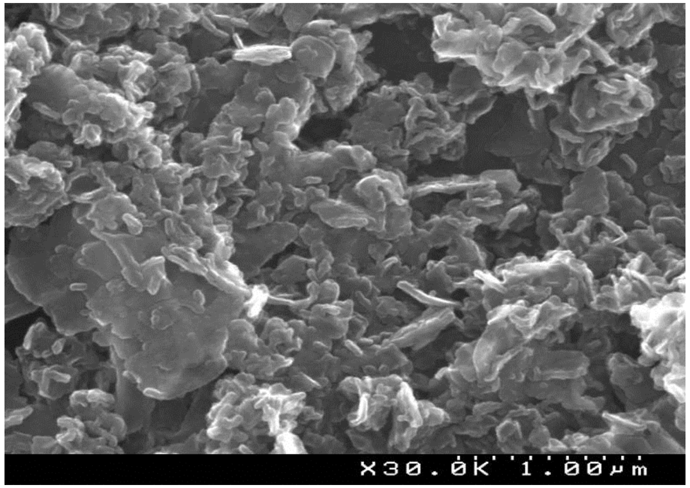
D.G.Shchukin,S.V.Lamaka,K.A.Yasakau,M.L.Zheludkevich,H.Möhwald,M.G.S. Ferreira, *JournalofPhysicalChemistryC*,112(2007)958-964.

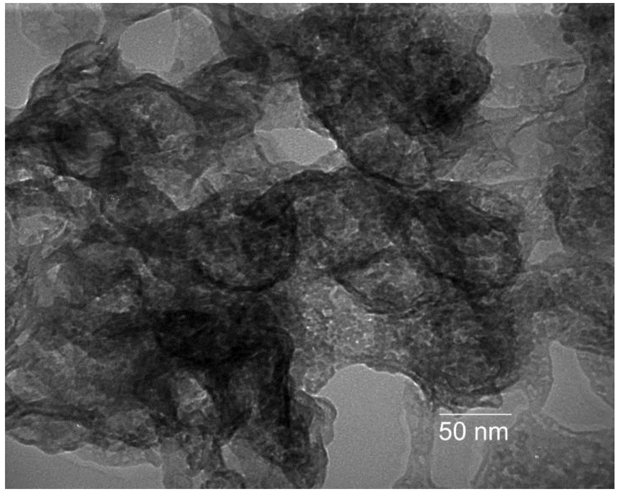
Example 2: LDH nanocontainers



Layered double hydroxide (LDH) powders

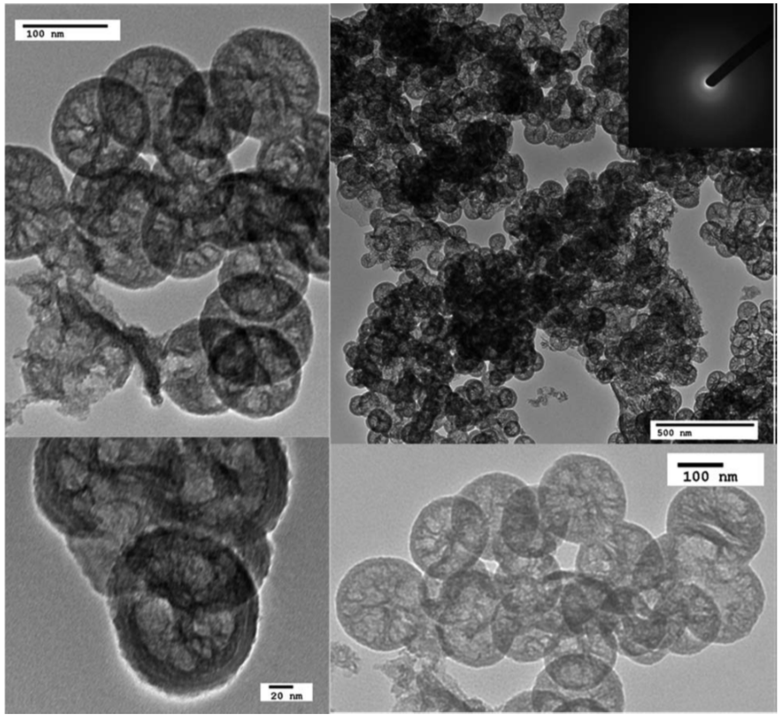
Inhibiting anions





S. K. Poznyak, J. Tedim, L. M. Rodrigues, A. N. Salak, M. L. Zheludkevich, L. F. P. Dick and M. G. S. Ferreira, ACS Appl. Mater. Interfaces, 2009, 1, pp 2353–2362

Example 3: SiO2 nanoparticles



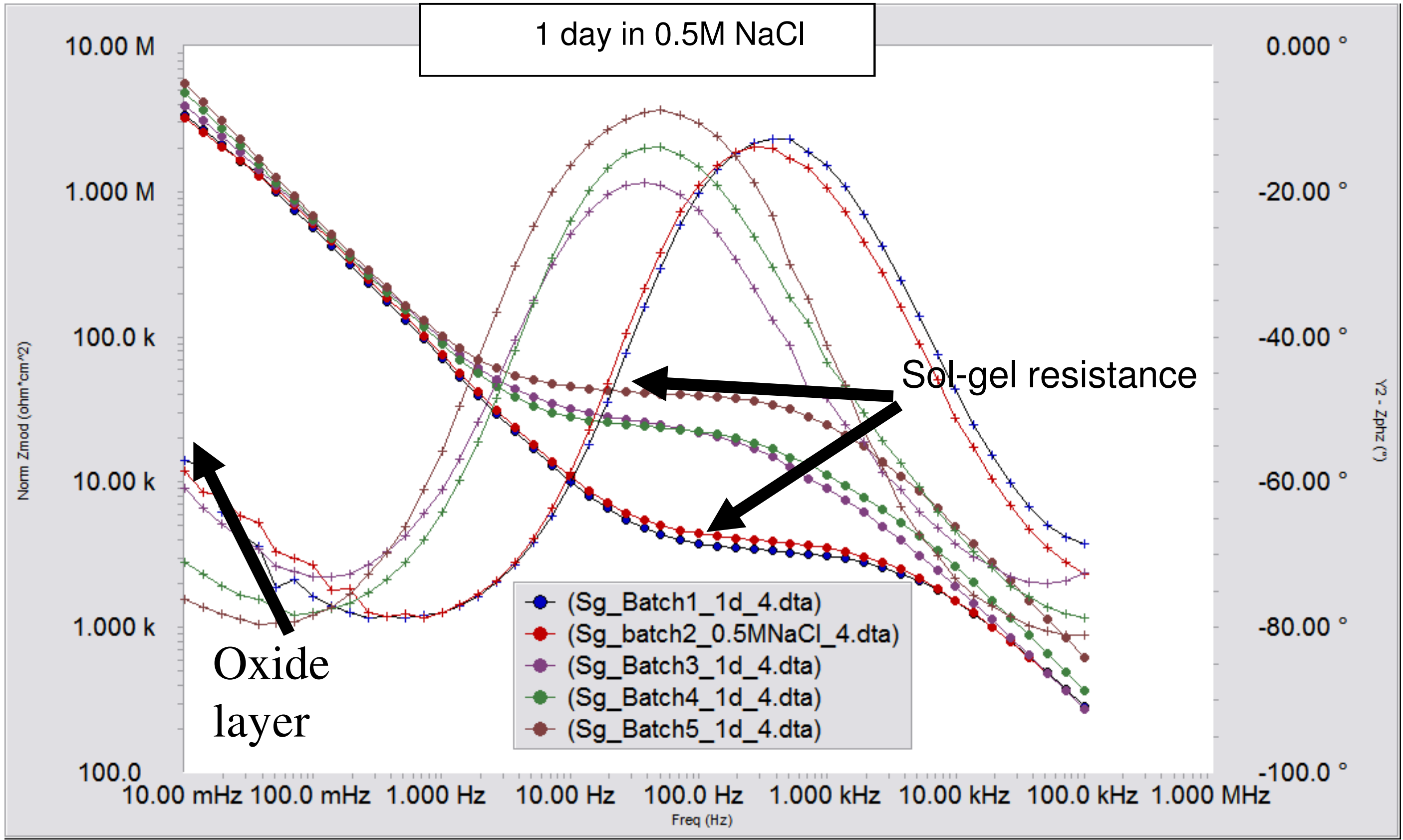
Frederico Maia, Joao Tedim, Aleksey D. Lisenkov, Andrei N. Salak, Mikhail L. Zheludkevich and Mario G. S. Ferreira, Nanoscale, 2012, 4, 1287

Sol-gel formulations

Name	Metalorganic compound	Complexant	Acidified water (HNO3) for hydrolysis	Hybrid silanes	Solvent
Batch 1	TPOZ 2.24 ml	EthAcAc 2.24 ml	H2O pH(0.5) 1.17 ml	GPTMS 5.52 ml	2-Propanol 5.52 ml
Batch 2	TPOZ 2.24 ml	EthAcAc 1.61 ml	H2O pH(0.5) 1.17 ml	GPTMS 5.52 ml	2-Propanol 5.52 ml
Batch 3	TPOZ 2.24 ml	EthAcAc 2.24 ml	H2O pH(1) 1.8 ml	GPTMS 5.52 ml	2-Propanol 5.52 ml
Batch 4	TPOZ 2.24 ml	EthAcAc 2.24 ml	H2O pH(0.5) 1.8 ml	GPTMS 5.52 ml	2-Propanol 5.52 ml
Batch 5	TPOZ 2.73 ml	EthAcAc 1.96 ml	H2O pH(0.5) 2.2 ml	GPTMS 6.74 ml	2-Propanol 3.37 ml

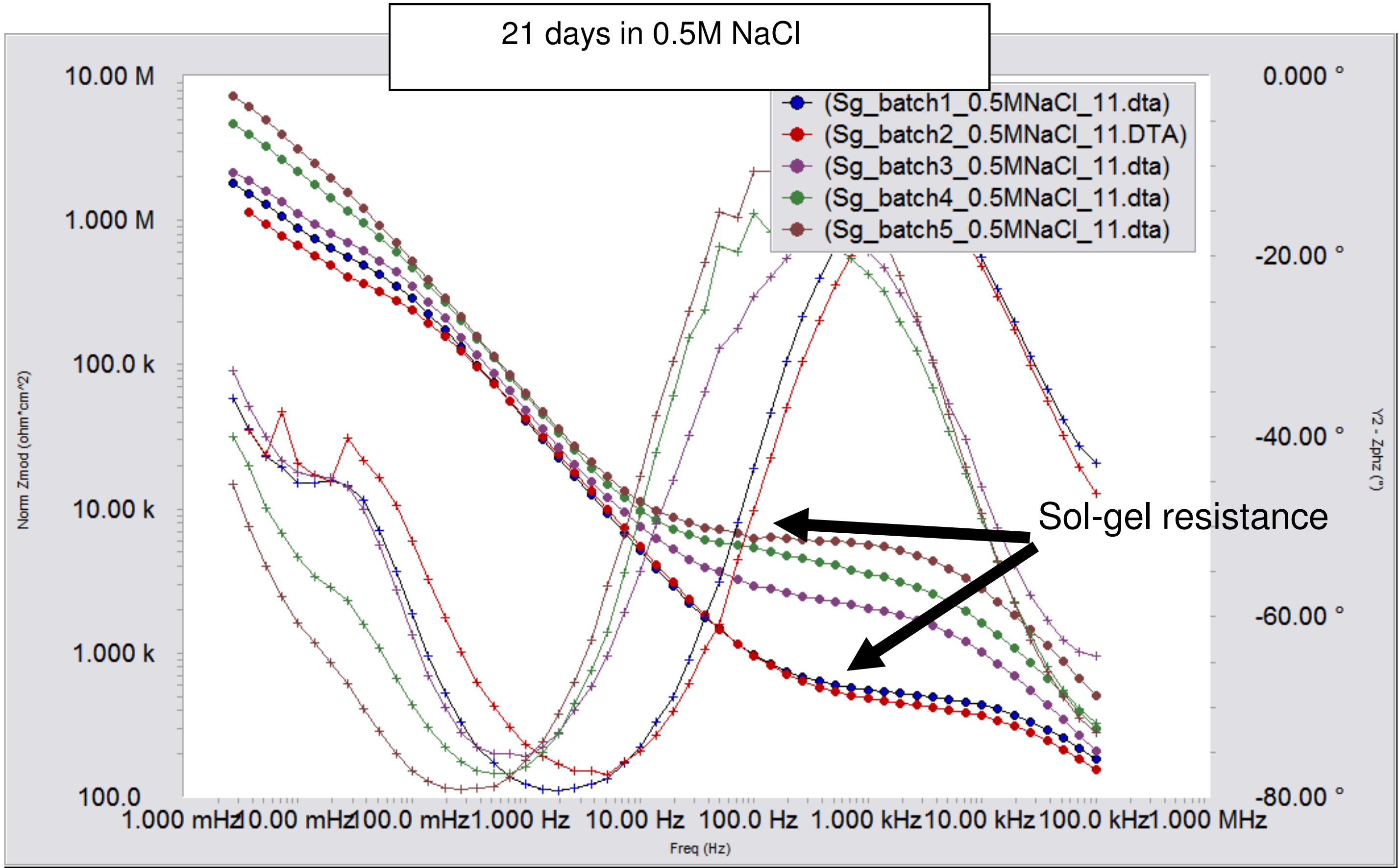
Table 1. Sol-gel formulations with modifications of complexant, H_2O and 2-propanol content

EIS results



✓ **Modified sol-gel coatings show higher barrier protection**

EIS results



- ✓ **At the end of immersion modified sol-gel have highest protection**

Optical photographs

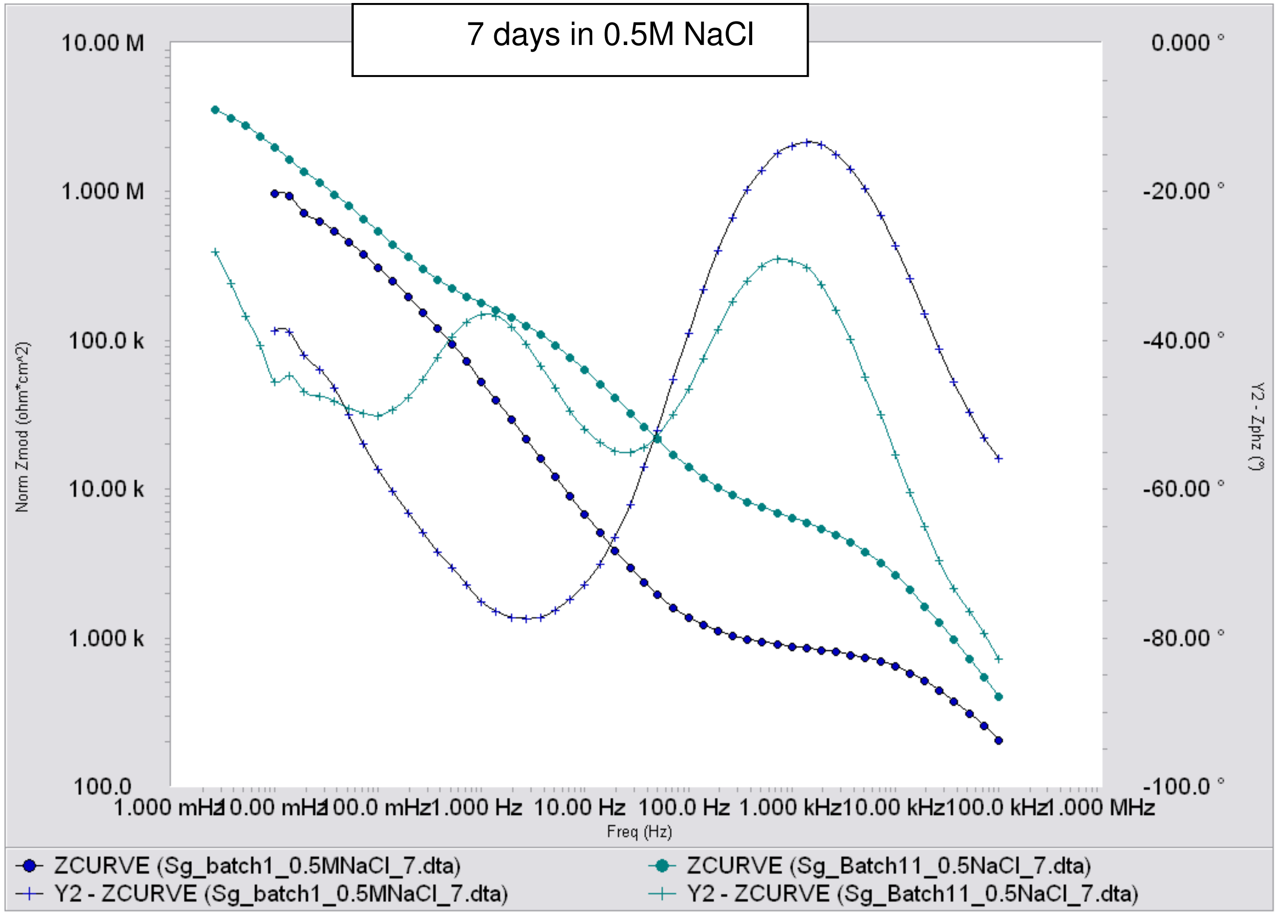
Batch 5: TPOZ+EthAcAc+pH(0,5) H_2O / GPTMS+ half amount of 2-propanol+pH(0,5) H_2O higher amount

Sol-gel formulations

Name	Me-organic compound	Complexant	Acidified water for hydrolysis	Hybrid silanes	Resin and crosslinkers	Solvent
Batch 11	TPOZ 2.42 ml	EthAcAc 2.42 ml	H2O pH(0.5) 1.27 ml	GPTMS PTMS	X	2-Propanol 5.5 ml
Batch 7	TPOZ 2.42 ml	EthAcAc 2.42 ml	H2O pH(0.5) 1.27 ml	GPTMS PTMS	1.7g DER 0.57 ml APS 1:5 NH2/epoxy	2-Propanol 5.5 ml
Batch 8	TPOZ 2.42 ml	EthAcAc 2.42 ml	H2O pH(0.5) 1.27 ml	GPTMS PTMS	1.7g DER 1.14 ml APS 1:2.5 NH2/epoxy	2-Propanol 5.5 ml
Batch 8+1 (aged 1 day)	TPOZ 2.24 ml	EthAcAc 2.24 ml	H2O pH(0.5) 1.8 ml	GPTMS PTMS	1.7g DER 1.14 ml APS 1:2.5 NH2/epoxy	2-Propanol 5.52 ml
Batch 9	TPOZ 2.42 ml	EthAcAc 2.42 ml	H2O pH(0.5) 1.27 ml	GPTMS PTMS	1.7g DER 0.082 ml Ethylenediamine 1:10 NH2/epoxy	2-Propanol 5.5 ml

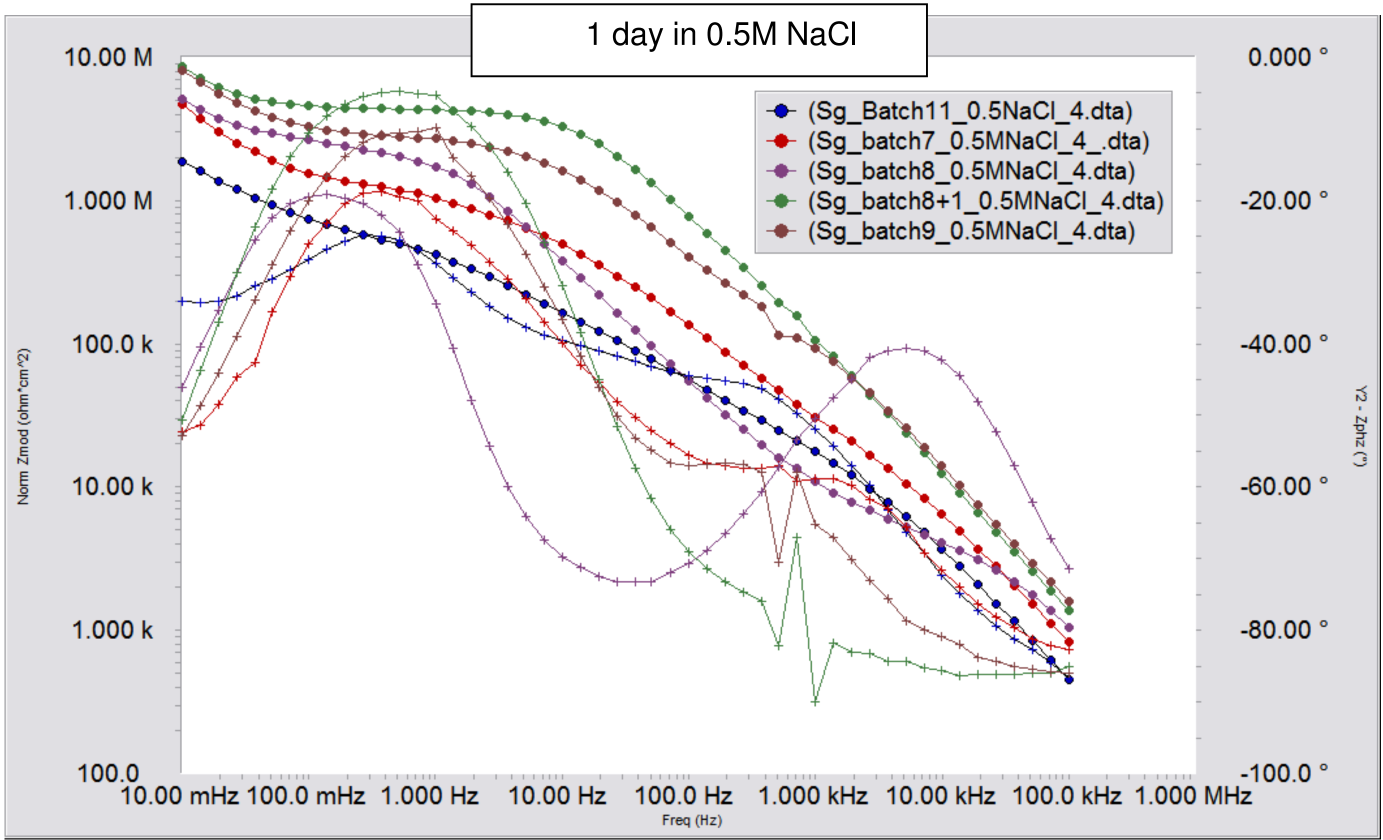
Table 2. Sol-gel formulations with and without cross linking additives

EIS results



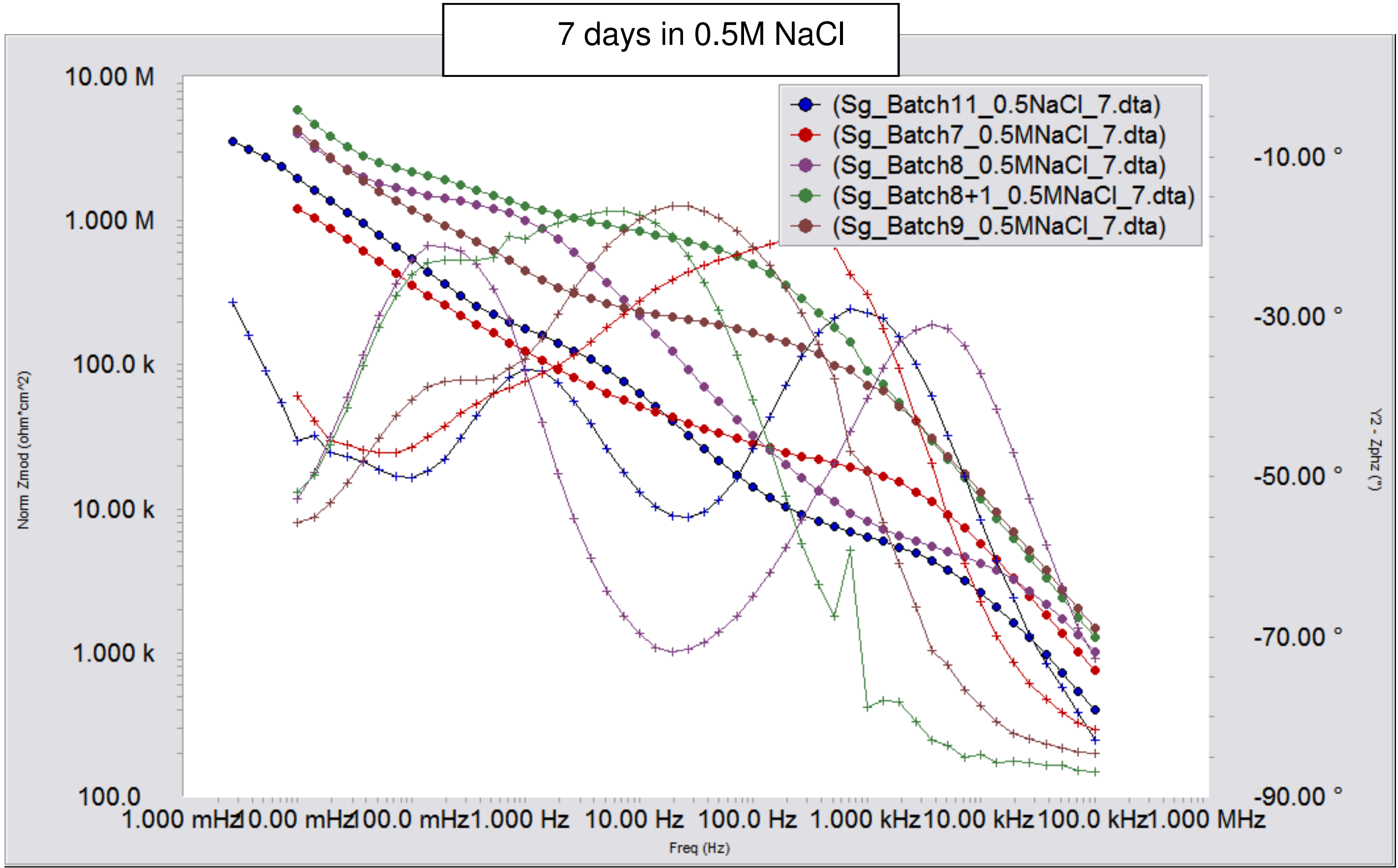
- ✓ **The impedance spectra demonstrate enhanced behavior of the modified system compared to standard sol-gel Batch 1**

EIS results



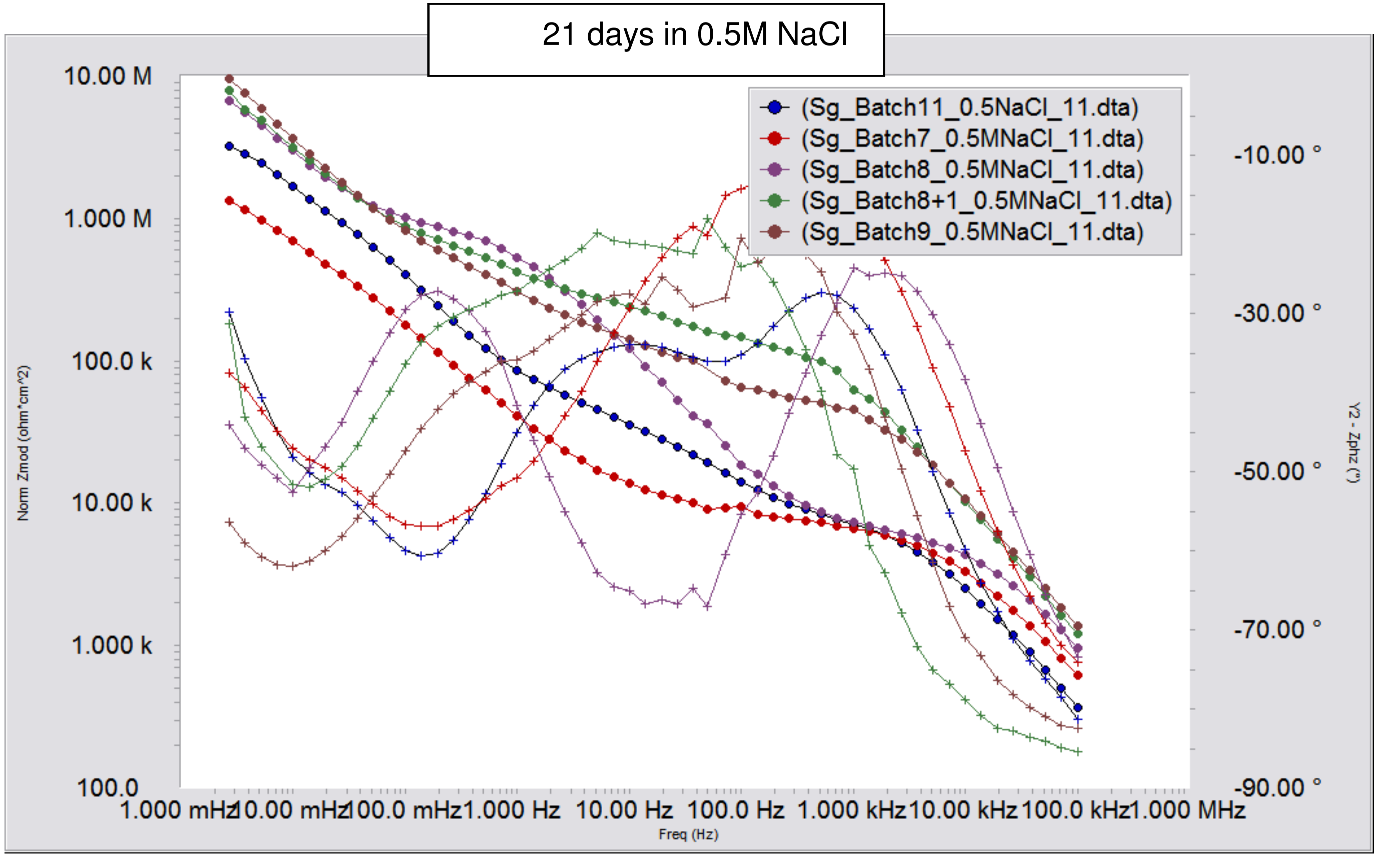
✓ **Modified sol-gel coatings show higher barrier protection provided by higher reticulation of sol-gel matrix with cross-linking additives**

EIS results



- ✓ **Higher amine concentration can lead to deterioration of coating properties (Batch 7)**

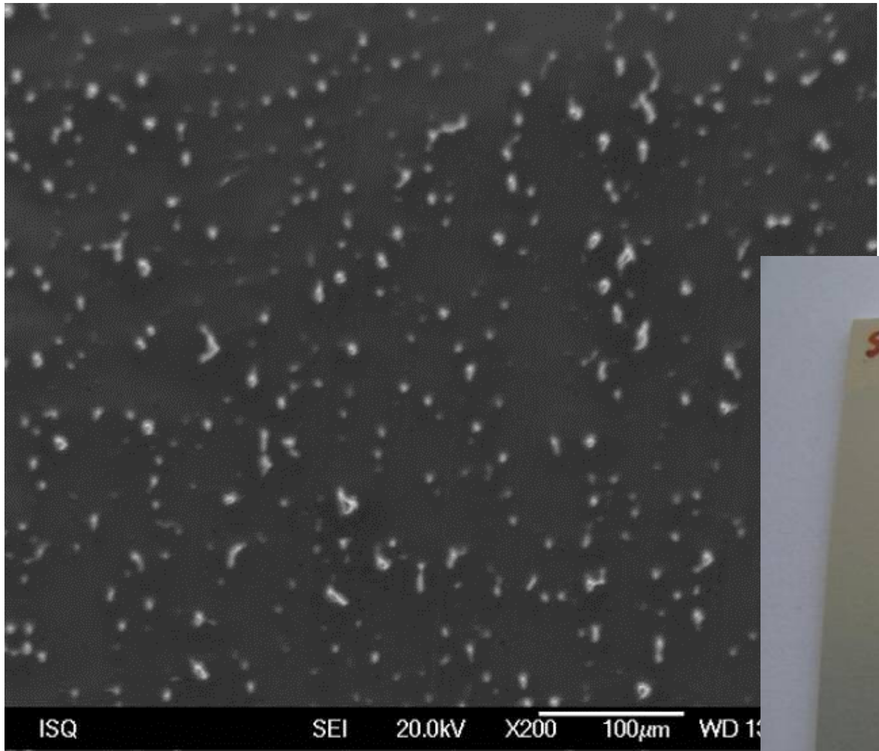
EIS results

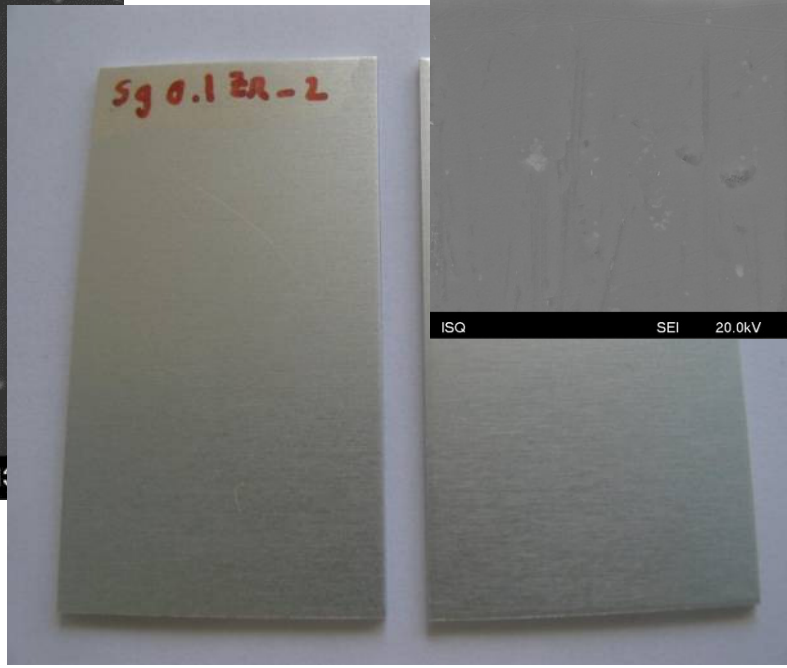


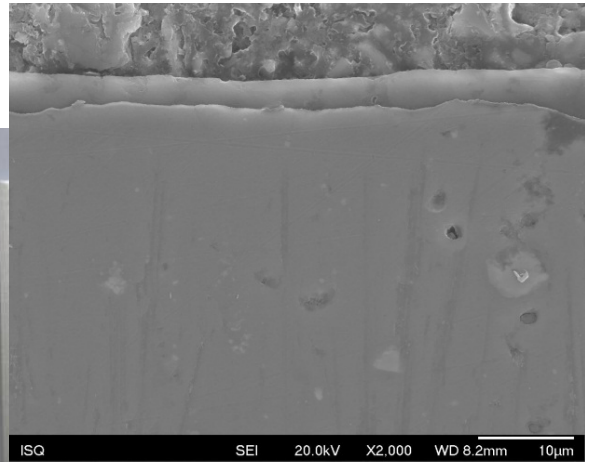
- ✓ **Sol-gel cross linking significantly improves barrier sol-gel properties and corrosion protection**

Optical photographs

SEM analysis







Aluminium samples coated with zirconium (Zr) hybrid films and SEM figures of coatings.

Salt Spray testing

1000 h 500 h 300 h

Illustrative picture of the samples, after salt spray test. (Hybrid film nº 5).

Coating Thickness

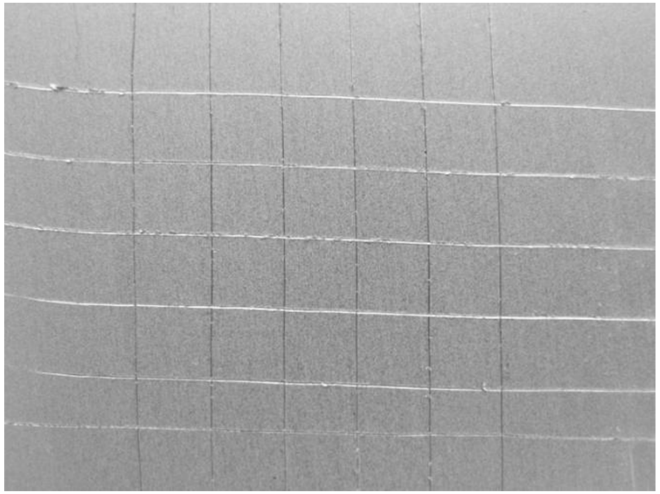
Magnetic Induction Method

(NP EN ISO 2808)

Minimum, maximum and average values of coatings thickness.

Coating	Coating Thickness (µm)			
	Minimum	Maximum	Average	σ
Hybrid Film nº1	4,0	5,3	4,6	0,6

Adhesion Test



Illustrative picture of coating adhesion test.

Preliminary Conclusions

- ✓ Variation of the ratios of 2-propanol, complexant and water was studied for hybrid epoxy based sol-gel system.
- ✓ increase of the water ratio and decrease of 2-propanol and Ethylacetoacetate is beneficial for the condensation degree of the sol-gel coating and for corrosion protection of the underlying metallic substrate.
- ✓ The use of different crosslinking additives such as APS, Ethilendiamine, Epoxy resins can also be used for increase of the sol-gel matrix barrier properties.
- ✓ In some points, the additional ageing of the sol-gel formulation before coating application can be used to enhance properties of the coatings.

Sol-gel films + nanocontainers loaded with inhibitor

Different type of nanocontainers with inhibitors, such as LDH, SiO2 nanoparticles and HS will be added to the optimized sol-gel formulation, in the last sol-gel synthesis step in reactor 3.

Inhibitor:

- mercaptobenzothiazole anions (MBT)

Scale up

- The developed formulations will be up-scaled in close collaboration with a SME (Aerohelice).
- Aerohelice will create demonstrators and coat them with the developed multifunctional pre-treatments.
- The demonstrators will be then painted and tested using standard methods in respect to the requirements.

Scale up

- Produce larger volumes of solution (1 l)
- Evaluate coatings performance
- Control the bath stability (pot life)
- Design of tanks for industrial application (pilot installation)
- Construction of the pilot installation at a SME facilities
- Coating application (spray)
- Scale up the selected formulations
- Coating the demonstrators
- Evaluation of the corrosion resistance

The industrial work is carried out using standard methods in respect to the requirements.

Acknowledgements

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QREN / FEDER

Pré-tratamentos Sol-Gel NAnoesTruturados para Ligas de ALuminio Utilizadas em Aeronáutica (NATAL)

Eureka Project

Multifuntional NAnostructured pre-Treatments for Strutural ALuminium Alloys (NATAL)
Billateral Technological Cooperation between Portugal and Israel (The EUREKA Programme)

Thank you

for your attention!

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